THE EXAMINATION OF KINOS AS AN AID IN THE DIAGNOSIS OF EUCALYPTS.

PART L.-THE RUBY GROUP.

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The astringent exudations so common on species of Eucalyptus are termed Kinos. The author is not aware that these substances have hitherto been taken cognisance of in the elucidation of species, and he proposes to give a brief account of his experiments in this direction. The genus Eucalyptus is such an abnormally difficult one, that any method of showing the affinities of its species must be welcome.

The author has already shown (*Pharm. Journ.* [3], XX. p. 221) that Eucalyptus Kinos may readily be grouped into three great classes, according to their behaviour with water and with spirit. Briefly, he divided them into (1) The Ruby Group, which consists of ruby-coloured Kinos, the members of which are soluble either in cold water or in cold spirit; (2) The Gummy Group, whose members are soluble in cold water, but very imperfectly in spirit, owing to the gum they contain; (3) The Turbid Group, whose members are soluble in hot water or in hot alcohol, but the solutions become turbid on cooling; all the members of this group contain catechin.

The author, however, wishes to make it quite clear that these Groups only refer to Kinos which he has actually examined, since he does not presume that the Kinos he has never seen fall into either one of them, whatever his opinion may be in regard to some of those yet undescribed. It is very possible that fresh groups and sub-groups showing affinities of Kinos may yet require to be erected, but the material at his disposal at present does not justify him in making other than the three broad groups already alluded to.

Bentham (following Mueller, Fragm. ii.), in the Flora Australiensis, classified the Eucalypts according to the shape of their anthers. The Renantheræ, those with kidney-shaped anthers, comprise the following species found in New South Wales:—

E. stellulata, Sieb.

E. pauciflora, Sieb.

E. regnans, F.v.M.

E. amygdalina, Labill.

E. obliqua, L'Hérit.

E. stricta, Sieb.

E. macrorrhyncha, F.v.M.

E. capitellata, Sm.

E. eugenioides, Sieb.

E. piperita, Sm.

E. pilularis, Sm.

E. triantha, Link (Syn. E. acmenioides, Schau.)

E. haemastoma, Sm.

E. Sieberiana, F.v.M. (Syn. E. virgata, Sieb.)

E. microcorys, F.v.M.

With the exception of that of *E. triantha*, the author has examined the Kinos of all the above species, including those of innumerable individuals belonging to species found in the Counties of Cumberland, Camden and Cook. It is rather remarkable to find that, with one exception (*E. microcorys*), the whole of the Kinos in the Renantheræ belong to the Ruby Group. The author also has arrived at some unexpected results in connection with the other two groups, but he does not propose to deal with those in the present paper.

E. microcorys has quite an anomalous Kino, that is to say, it can readily be distinguished from all others. Unlike the Ruby Kinos it is very friable (capable of being crushed to a fine powder between the fingers, which no "ruby" Kino ever is), and looks like a parcel of uncut garnets. It forms an orange-brown powder, and belongs to the Turbid Group. At present it may be compared to "the exception which proves the rule." It is, however, worthy of

note that *E. microcorys* is not placed by Bentham in the Renantheræ, but in a group called by him Heterostemones, in which he includes an additional member of Baron Mueller's Renantheræ, the other members falling in the Baron's Porantheræ.

. The author has proved by experiments on many samples that a Kino of one species, no matter what its variety, and under whatever circumstances of climate, soil, &c., it may grow, invariably belongs to one group.* For example, all the Kinos of perhaps twelve specimens of eight varieties of E. amygdalina Kino which have passed through his hands belong to the Ruby group, and not one to either the Gummy or the Turbid group. The composition of all Kinos appears to be constant to that extent. Since this discovery dawned upon the writer, he has had many opportunities of verifying its truth; in some notable instances where Kino has been forwarded to him, he has been able to call the naming of the species in question, and by assigning the group to which it belongs has thrown light upon its position, and has caused the evidence on which a speciesname had been given to be re-opened, with the result, in each case, of alteration. He therefore does not hesitate to strongly recommend that in sending specimens of little known or variable Eucalypts to be named, the Kino, wherever procurable, should always form portion of the material for the botanist to work upon.

The author offers his chemical system of grouping Eucalypts merely as a supplement to, or a check upon, the anthereal

^{*} In the amplified anthereal grouping of Bentham, the following species are placed by him in more than one series or sub-series:—

E. virgata (Sieberiana).

E. bicolor (largiflorens).

E. stricta.

E. albens (hemiphloia).

E. siderophloia.

E. gomphocephala.

At the same time, it is but fair to point out that in Baron Mueller's anthereal classification no Eucalypt appears in more than one group, of which, however, there are but three for the whole genus.

system. Often Kino cannot be found on a certain tree; on the other hand, the uncertain period of flowering of many species often precludes any examination of anthers. And when anthers are obtained, only those who have frequently examined the flowers of this genus know how difficult and uncertain it is to assign the species yielding them to its proper anthereal group. When once the Kino is obtained, however, an ordinary child of seven would be able accurately to place it in its proper group.

The specimens of Kino now, and to be, described are the property of the Committee of Management of the Technological Museum, in which collection will be found many specimens collected by Mr. Bäuerlen on behalf of the Committee, over forty specimens collected by the author, together with a few of miscellaneous origin, the whole forming a series probably not to be equalled anywhere,

It will be seen from the descriptions now given how similar are all the Kinos of this Ruby group. Time seems to alter them all similarly; and the author believes that Kinos of all these species, provided the same period has elapsed since exudation, and they have been exposed to similar climatic influences, tend to have precisely the same appearance and composition. He has given a few notes on the appearance of those of different species partly with a view to bring out the relationship between physical appearance and chemical composition, and partly with the view to furnish the fullest particulars in regard to these little-known substances. It must be borne in mind that the dates given are either those of collection or of receipt, and not of exudation, so that they do not, in many cases, give a precise idea of their comparative ages. But appearance and composition of the Kinos give, he believes, an infallible clue to their ages. With not much diffidence he hazards the belief that when a series of Kinos just exuded shall have been collected, and thus their ages known at the time of different experiments, it will be found that the percentages of tannic acid, for instance, will be in inverse ratio to their ages.

EUCALYPTUS AMYGDALINA, Labill., B.Fl. iii. 202 (Syn. E. fissilis, F.v.M.; E. radiata, Sieb.; and other synonyms).

This Eucalypt has more than a score of vernacular names, but in regard to this species, as in others, only those vernacular names have been used which are actually employed to describe the tree in the locality given.

Found in Tasmania, Victoria, N. S. Wales.

1. E. amygdalina var. radiata. "Ribbon Gum." Nelligen, Clyde River, N.S.W. Collected 21st and 22nd September, 1886. Height, 100-120 ft.; diam., 2 ft. 6 in.

A clear port-wine coloured Kino, which is fairly friable, yielding a sparkling powder. It is not readily obtainable in large pieces. It dissolves readily in cold water, forming a clear, medium ruby liquid, but the residue contains more woody matter than the Bombala sample, and less phlobaphene. Colour of residue Vandyke brown.

(Note.—Colours are taken from damp residues. The colours of aqueous solutions were taken from $\frac{1}{2}$ gram, of powdered Kino in 100 cc. of water, which stood for three days, and the colour estimated by placing the liquid in a bottle 2 inches in diameter.)

Kino-tannic acid, 62.95 per cent.; insoluble phlobaphenes, 6.46 per cent.; soluble in cold water, 92.54 per cent.*

2. E. amygdalina, var. "Peppermint." Bombala, N.S.W. Collected 14th Feb., 1887. Height, 60-80 ft.; diam., 3 ft. Physical description same as No. 1.

In cold water it forms a solution of a pale ruby colour. The insoluble phlobaphene is very dark, almost black. Colour of residue purplish-brown.

^{*}The remainder of these Kinos consists for the most part of hygroscopic moisture (average 20 per cent.), together with small percentages of sugar, resin, &c. I have made complete analyses of them, but the descriptions of the raw products themselves, and an account of the botanical questions involved in the elucidation of them, can alone properly be brought before this Society.

Kino-tannic acid, 62.58 per cent.; insoluble phlobaphenes, 6.58 per cent.; soluble in cold water, 92.62 per cent.

3. E. amygdalina, var. "Peppermint." (This and the preceding tree are very different in appearance.) Little River, near Braidwood, N.S.W. Collected 11th November, 1886. Height, 60-80 ft.; diam., 1-2 ft. Physical description same as "Ribbon Gum."

To cold water it yields a perfectly clear pale ruby solution, with insoluble phlobaphene of the same colour. Residue contains a few particles of ligneous matter. Colour of residue Vandyke brown.

Kino-tannic acid, 62·4 per cent.; insoluble phlobaphenes, 5·5 per cent.; soluble in cold water, 93·4 per cent.

Following is the description of a sample of *E. amygdalina* Kino examined by Dr. Wiesner (Pharm. Journ. [3] ii. 102):— "Easily soluble in water, solution neutral, onion-red, turbid * on cooling. Black particles, and only in very thin fragments, zircon-red in transmitted light, fatty lustre, very tough, rich in fibrous bark."

4. This sample had been collected for an indefinite period when received on 29th December, 1887. No particulars are available.

This and the following Kino, received from the Sydney Botanic Gardens, are very similar in outward appearance, and the same description will apply to both. They have obviously been collected for a very considerable period, are bright and black, and look very much like little pieces of jet. Although of a horny nature, it is not very difficult to reduce them to a coarse black sparkling powder, as they are rather brittle, but it is very difficult to rub them down into an impalpable powder, which is dull, and in colour purplish-brown with a predominance of red, and inclining to Venetian red.

^{*} There is some mistake here; his labels have probably got mixed. I have examined scores of Kinos of this species. The same remarks also apply to E. pilularis, infra, a common Sydney species.

Cold water acts with extreme slowness upon this Kino, and a dark ruby liquid is the result, with nearly black insoluble phlobaphenes. The soluble phlobaphenes possess very powerful colouring properties.

Kino-tannic acid, 35.78 per cent.; insoluble phlobaphenes, 35.8 per cent.; soluble in cold water, 55.4 per cent.

5. Sample sent as *E. fissilis*. For physical description see previous specimen (No. 4). Cold water yields a dark ruby solution inclining to orange. The Kino dissolves slowly, leaving a residue of phlobaphene almost entirely of a rich red-brown colour, with but a very small proportion of black.

Kino-tannic acid, 30.59 per cent.; insoluble phlobaphenes, 40.9 per cent.; soluble in cold water, 50.1 per cent.

Following is Dr. Wiesner's description of a sample of *E. fissilis* Kino examined by him:—"Reddish solution, neutral, remaining clear on cooling, trace of gum-resin. Tough drops, blackish red, zircon-red, translucent, fatty lustre on fracture."

6. E. amygdalina, var. No local name. Appears to be scarce. Has a bark something like "Mahogany" (E. robusta). Cambewarra, N.S.W., 30th May, 1888. Height, 60-80 ft.; diam., 2-3 ft.

The greater portion of the small sample obtained has evidently remained long on the trees. A few freshly exuded drops are of a clear reddish-brown colour; the remainder is so opaque that its colour by transmitted light can scarcely be determined, though at the edges of some pieces a reddish-brown colour is observed. The general colour by reflected light is Vandyke brown, and the Kino cuts like horn.

Cold water forms a pale orange-brown solution. It is, however, all but insoluble. Alcohol (B.P. strength of tincture) yields a pale brown liquid, and a granular almost black residue of phlobaphenes.

This sample is chosen as an example of the effect of age on a ruby Kino. The tendency to insolubility has proceeded to an even greater extent in the case of the specimen which follows (No. 7).

Kino-tannic acid, $12\cdot4$ per cent.; insoluble phlobaphenes, $60\cdot5$ per cent.; soluble in cold water, $24\cdot2$ per cent.

7. E. amygdalina, var. "Messmate." Nowra, August, 1888. Height, 100-150 ft.; diam., 2-6 ft.

This sample has also been chosen to illustrate the effect of extreme age on a ruby Kino. It has been obtained from the interior of the wood, and incrusts or is attached to the chamoisleather fungus (Xylostroma giganteum, Fries). It bears a remarkable resemblance to vulcanite, but it is scarcely of a pure black, being of a uniform Vandyke brown. Its fracture is conchoidal, and of an "egg-shell black." It is about as hard as vulcanite, and its powder (difficult to obtain on account of the toughness of the material) is of a burnt-umber colour. It yields practically nothing to boiling water, alcohol or ether, and consists almost entirely of phlobaphenes.

8. E. amygdalina, var. (near E. regnans, F.v.M.). "Cut-tail," "Bastard Black-butt." Tingiringi Mountain, Delegate, N.S.W., 2nd March, 1889. Height, 200-300 ft.; diam., 3-6 ft.

A fresh Kino which appears in no way to differ from that of fresh normal E. amygdalina.

EUCALYPTUS EUGENIOIDES, Sieb. Made a variety of E. piperita in B. Fl. iii. 208.

Found in Victoria and N. S. Wales.

9. "Broad-leaved Stringybark." Bangley Creek, Cambewarra, 15th March, 1888. Obtained from various trees from 60-80 ft. high, and 1-2 ft. in diam. Kino very scarce.

This has been quite freshly exuded, and is for the most part of a pale ruby colour, although particles of it are of deeper tint. It

is transparent and bright-looking, and easily powdered. Fragments of the very fibrous bark are usually attached to the pieces.

In cold water it forms a clear solution of a pale ruby colour. Residue Vandyke brown.

Kino-tannic acid, 65·48 per cent.; insoluble phlobaphenes, 3·6 per cent.; soluble in cold water, 96·0 per cent.

10. "Broad-leaved Stringybark." Bangley Creek, Cambewarra, 29th March, 1888. Height, 40-60 ft.; diam., 1-2 ft.

This specimen was obtained in the same neighbourhood as the preceding one, but it is by no means so fresh-looking, having obviously remained on the trees for a much longer time.

Cold water yields a medium ruby liquid. Colour of residue Vandyke brown.

Kino-tannic acid, 59.37 per cent.; insoluble phlobaphenes, 7.5 per cent.; soluble in cold water, 91.6 per cent.

11. "Stringybark." Between the Valley and Springwood, Blue Mountains, N.S.W., 3rd April, 1888. Height, 60 ft.; diam., 1 ft.

Kino of this species is difficult to collect, like that of other stringybarks, as it becomes firmly cemented to the fibrous bark. It is something like *E. obliqua* Kino, but perhaps more similar in appearance to that of *E. piperita* from the same locality. It is intermediate in toughness between the two Kinos. Colour of powder purplish-brown.

Cold water forms a medium ruby liquid, inclining to reddishbrown. Residue dark brown.

Kino-tannic acid, 64·26 per cent.; insoluble phlobaphenes, 2·5 per cent.; soluble in cold water, 97·0 per cent.

12. "Stringybark." Barney's Wharf, Shoalhaven, N.S.W., August, 1888. Height, 60-80 ft.; diam., 2-3 ft. Freshly exuded; of a rich ruby colour. Yields a pale ruby liquid to cold water.

Kino-tannic acid, 65.46 per cent.; insoluble phlobaphenes, 2.9 per cent.; soluble in cold water, 96.4 per cent.

EUCALYPTUS HÆMASTOMA, Smith, B.Fl. iii. 212.

Found in Tasmania, Victoria, N. S. Wales and Queensland.

The specific gravity of a sample of Queensland Kino from this species is about 1.378, and the percentage of tannin 64.51, according to Mr. Staiger.

13. Rough or Small-leaved "Stringybark." Lyttelton (Colombo), Candelo, N.S.W., 24th December, 1886. Height, 40-60 ft.; diam., 2 ft.

When freshly exuded this Kino is of a clear light ruby colour, becoming more or less opaque and of a Vandyke brown colour, like other ruby Kinos, if it remains sufficiently long on the trees. It is clean to handle, powders fairly readily, forming a light purplish-brown powder. In cold water it forms medium ruby-coloured liquid. Colour of residue Vandyke brown.

Kino-tannic acid, 57.35 per cent.; insoluble phlobaphenes, 11.4 per cent.; soluble in cold water, 88.0 per cent.

14. Received from Mr. F. M. Bailey, Government Botanist of Queensland, 28th February, 1888, but no particulars are available. It is in rather larger and more rounded pieces than the sample from Colombo, and has evidently been collected for a longer period than the former. It is bright-looking, and of such a deep garnet colour as to be almost opaque.

To cold water it yields a solution of a medium ruby colour with a little brown in it. Residue Vandyke brown.

Kino-tannic acid, $59\cdot92$ per cent.; insoluble phlobaphenes $11\cdot76$ per cent.; soluble in cold water, $87\cdot8$ per cent.

EUCALYPTUS MACRORRHYNCHA, F.v.M., B.Fl. iii. 207.

Found in Victoria and N. S. Wales.

15. "Stringybark." Amboyne, Delegate, N.S.W., 25th May, 1887. Height, 80-120 ft.; diam., 2-4 ft.

Of a rich ruby colour. This particular sample is rather friable, and for this reason appears of a dull colour, unless it has been very little handled. It reminds one somewhat of some specimens of seed-lac.

To cold water it yields a medium ruby-coloured solution. The residue contains particles of fibrous bark, together with phlobaphene of a dark ruby colour. Residue Vandyke brown.

Kino-tannic acid, 64.4 per cent.; insoluble phlobaphenes, 5.52 per cent.; soluble in cold water, 93.78 per cent.

EUCALYPTUS OBLIQUA, L'Hérit., B.Fl. iii. 204 (Syn. E. gigantea, Hook. f.; and other synonyms.)

Found in South Australia, Victoria, Tasmania, and N. S. Wales.

Following are the results of Dr. Wiesner's examination of two Kinos of this species:—

- "E. gigantea. Little soluble in water; solution brownish, neutral, no turbidity, rich in gum-resin. Tough, drop-like pieces, of a zircon red.
- "E. obliqua. Taken as identical with E. gigantea. Completely soluble in water, with deep red colour, neutral, no turbidity, free from gum-resin. Looks like Kino. . . .
- "E. gigantea. Add to solution first HCl and then NH₄ HO, yellowish-red ppt, which on exposure to the air becomes of rusty red.
 - " E. obliqua. Dark violet ppt under the same circumstances." The first sample was evidently much older than the second.
- 16. "Stringybark." (Botanic Gardens, Sydney, received 29th December, 1887.)

Another Kino which must have been collected for a very long period. It looks perfectly black by reflected light, and has much the appearance of jet. It is fairly brittle, but rather difficult to reduce to an impalpable powder, which is rich Vandyke brown in colour.

Cold water yields a clear dark reddish-brown solution. The phlobaphene residue is very abundant, and almost a perfect model of the original Kino.

Kino-tannic acid, 21·4 per cent.; insoluble phlobaphenes, 48·52 per cent.; soluble in cold water, 38·9 per cent.

15

EUCALYPTUS PAUCIFLORA, Sieb. (Syn. E. coriacea, A. Cunn., the species name in B.Fl. iii. 201, and a more correct one than Sieber's.)

17. "Cabbage Gum." Monga, near Braidwood, 1st and 2nd October, 1886. Height, 60-80 ft.; diam., 1-2 ft. A free yielder of Kino in this district.

This Kino is rather tenacious, adhering to pestle and mortar, and yielding a dull orange-tinted powder. It dissolves readily and almost entirely in cold water, forming a medium ruby liquid, with a garnet residue.

Kino-tannic acid, 55·37 per cent.; insoluble phlobaphenes, 8·6 per cent.; soluble in cold water, 91·8 per cent.

EUCALYPTUS PILULARIS, Smith, B.Fl. iii. 208.

Found in Victoria, N. S. Wales, and Queensland.

Following are Dr. Wiesner's remarks on a sample of this Kino:—

"Readily soluble in water, red solution, faintly acid, turbid * on cooling, traces of gum-resin. Pieces opaque, earthy, or with slight fatty lustre, dark reddish-brown."

18. "Blackbutt." Eastwood, near Sydney, 28th April, 1888. Height, 50 ft.; diam., 1 ft.

In outward appearance this Kino so closely resembles the sample *E. piperita* (Valley), as to be scarcely distinguished from it.

Cold water dissolves it readily, forming a quite clear liquid. Like very new Kinos it has a purplish rose tint. Colour of residue Vandyke brown.

Kino-tannic acid, 65.52 per cent.; insoluble phlobaphenes, 2.8 per cent.; soluble in cold water, 96.4 per cent.

^{*} There is some mistake here.

EUCALYPTUS PIPERITA, Smith, B.Fl. iii. 207.

Found in Victoria and N. S. Wales.

Dr. Wiesner says of a sample :—

"Easily soluble in water; solution yellowish-red, neutral, free from gum-resin. No turbidity on cooling. Dense pieces of zircon-red, translucent."

19. E. piperita, var. "Messmate," or "Narrow or Almond-leaved Stringybark." Brooman, Clyde River, N.S.W., 14th September, 1886. Height, 100-120 ft.; diam., 2-3 ft.

One of the clear ruby or garnet Kinos. Some of it is in rather large pieces, and is rather hard and tough. It has a very bright fracture.

Cold water dissolves it to a medium ruby-coloured liquid, leaving a residue consisting chiefly of phlobaphenes. Colour of residue dark purplish-brown.

Kino-tannic acid, 59.78 per cent.; insoluble phlobaphenes, 8.7 per cent.; soluble in cold water, 90.84 per cent.

20. "Stringybark." The Valley, near Springwood, N.S.W., 4th April, 1888. Height, 80 ft.; diam., 4 ft.

The description given of the Brooman sample (No. 18) applies here exactly. The only perceptible difference is that the specimens from the Valley are a little lighter in colour because fresher. It is very tough to powder, and can be cut in pieces with a knife.

Except that it is rather more easy of solution, to be accounted for by its more recent collection, this sample behaves exactly like the Brooman sample when in cold water. Colour of residue Vandyke brown.

Kino-tannic acid, 62.91 per cent.; insoluble phlobaphenes, 5.1 per cent.; soluble in cold water, 94.1 per cent.

21. "Peppermint," "Messmate." Barney's Wharf, Shoalhaven N.S.W., August, 1888. Height, 60-80 ft.; diam., 2-3 ft.

A rather handsome Kino. Freshly exuded, of a pale ruby colour; a portion of it is in very thin fragments, and shows a colour like orange lac. Much of it has been allowed to flow into a vessel and therefore is nearly pure.

Cold water yields a very pale ruby solution with a tint of rose. Colour of residue brown.

Kino-tannic acid, 67.52 per cent.; insoluble phlobaphenes, 4.0 per cent.; soluble in cold water, 95.4 per cent.

EUCALYPTUS SIEBERIANA, F.v.M. (Syn. E. virgata, Sieb., the species name in B.Fl. iii. 202).

Found in S. Australia, Tasmania, Victoria, and N. S. Wales.

- 22. "Mountain Ash." I have obtained a sample of Kino from this species (Mt. Victoria, N.S.W., March, 1889), which is an ordinary ruby Kino, both in appearance and chemical deportment.
- 23. "Mountain Ash," "Black Ash." A second sample of Kino of this species is from Tantawanglo Mountain, near Candelo, N.S.W., and is from a tree 60-80 ft.; diam., 2-6 ft. It was collected 12th July, 1889. It has exuded for a much longer time than the preceding sample. Neither has been quantitatively analysed.

EUCALYPTUS STELLULATA, Sieb., B.Fl. iii. 200.

Found in Victoria and N. S. Wales.

24. "Sally or Black Gum." Bombala, N.S.W., 17th Feb., 1887. Height, 30-50 ft.; diam., 2 ft.

A ruby Kino similar to most of the others in general appearance.

It yields a medium ruby liquid, with some phlobaphene residue and a few particles of woody matter. Colour of residue purplishbrown

Kino-tannic acid, 61.97 per cent.; insoluble phlobaphenes, 7.2 per cent.; soluble in cold water, 92.42 per cent.